The flash experiments were made at room temperature controlled at 23 ± 1 °C. The flash apparatus was of standard design;[21] half-duration and flash energy of the xenon flash lamp (Xenon Corp. N-851C) were ca. 10 μs and 150 J, respectively. A flash light in the range of 350–400 nm was selected by the use of appropriate light filters to prevent the excitation of alkenes. Kinetic observations of the thio radical were made with a continuous monitor light source and photomultiplier detector. The oxygen concentrations of solutions were calculated from Henry's law by dissolving oxygen under partial pressure after degassing the solution.[22]

Registry No. p-ClC_6H_4S, 31053-91-5; cyclopentene, 142-29-0; cyclohexene, 110-83-8; cycloheptene, 628-92-2; cyclooctene, 931-88-4; cyclododecene, 1501-82-2; 1,5-cyclooctadiene, 111-78-4; 1,3-cyclohexadiene, 592-57-4; 1,3-cycloheptadiene, 4054-38-0; 1,3-cyclooctadiene, 1700-10-3; cycloheptatriene, 544-25-2; cyclooctatetraene, 629-20-9; dicyclopentadiene, 77-73-6; bicyclo[2.2.1]-2-heptene, 498-66-8; bicyclo[2.2.1]hepta-2,5-diene, 121-46-0; methyl, 2229-07-4; bis(p-chlorophenyl) disulfide, 1142-19-4.

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Surface Photochemistry: Decomposition of Azobis(isobutyronitrile) on Dry Silica Gel[1]

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The generation of cyanopropyl radical pairs by the photolysis of azobis(isobutyronitrile) (AIBN) adsorbed on dry silica gel–benzene slurries has been investigated. The results require revision of an earlier observation that restrictions on the rotational motion of cyanopropyl radicals at a silica gel–benzene interface prevented the formation of the unsymmetrical coupling product dimethyl-N-(2-cyano-2-propyl)ketenimine. Both tetramethylsuccinodinitrile and the ketenimine were formed on the silica gel surface, even when dry, although the latter was partially hydrolyzed to the corresponding amide. Measurements of geminate recombination of radicals produced by direct photolysis of mixtures of deuterated and nondeuterated AIBN indicated that some radicals could escape, by translational motion, from their original geminate partners. The amount of translational motion was increased for the same cyanopropyl radical pair generated by triplet-sensitized AIBN decomposition. This latter observation supports the view that the triplet-sensitized decomposition of AIBN occurs *directly* from an excited state rather than by isomerization to a thermally labile cis isomer.

The behavior of both singlet and triplet spin-correlated radical pairs has been extensively investigated in solution.[2] It has been found that a geminate radical pair generated within a solvent cage has a number of pathways available to it: (1) it may react to form products either by recombination or disproportionation, or may recombined to regenerate starting material, (2) it may be transformed into a new radical pair, or (3) it may undergo diffusional separation to form free radicals. The first process can occur only with singlet radical pairs, whereas the latter two are independent of the radical pair multiplicity. Since intersystem crossing must precede geminate reaction of a triplet radical pair, processes 2 and 3 compete more effectively with process 1 from triplet than from singlet pairs. The amounts of geminate recombination may be varied by changing either the rate of intersystem crossing of the radical pair or the rate of its diffusional separation. The latter may be achieved by, for example, altering the viscosity of the medium. Changes in the relative importance of the above processes (1–3) are to be expected when the radical pair is generated in an environment where its motion is restricted, as, for example, in the crystalline state,[3] in a micelle,[4] or on a solid surface.[5,6] Variations in the amount of geminate radical pair reaction can provide a useful measure of such effects.

The behavior of adsorbed radical pairs and, in particular, the possibilities for their rotational and translational movement of inorganic surfaces such as silica gel, alumina, and porous Vycor have not been widely studied.[7] Similarly, there have been few studies of the photochemistry and mobility of adsorbed organic molecules, although the nature of the surface and the adsorbate–surface binding interaction have been extensively examined.

In the case of silica gel there are two types of surface functional groups: the siloxane and the silanol, as well as physisorbed water molecules.[13] It is generally accepted that for equilibrated surfaces there are $\sim$5 silanols/nm^2, but there has been no general consensus concerning the relative contributions from isolated, vicinal and geminal silanols.[14] The adsorption of organic molecules on silica is believed to occur through London dispersion forces, electrostatic interactions, and hydrogen bonding. The

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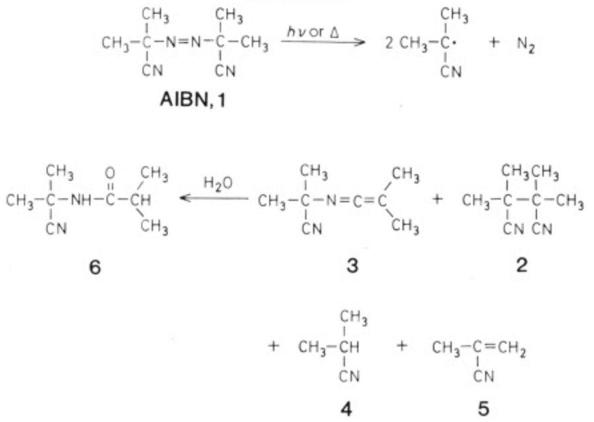
0022-3263/84/1949-0020$01.50/0

Scheme I



principal adsorption sites consist of surface silanols although siloxanes and hydrogen bonded water molecules may also be involved. In general, the nature and strength of the surface–adsorbate binding depend on both the activation treatment of the silica gel and the adsorbate polarity.[13] The variation of the site binding strength may well be attributed to the spatial arrangement of the silanols within pores (most of the surface area of porous silica gel is on the *inside*) so as to allow, for instance, multiple hydrogen bonding to the same molecule where permitted or solvation of an isolated silanol.

A number of ESR studies have attempted to examine the question of the mobility of adsorbed radicals.[8] Although the occurrence of both rotational and translational motion was postulated, these conclusions may be oversimplified since the effects of surface heterogeneity were not considered. Recently, however, limited translational motion has been shown to occur on dry silica gel and to precede recombination of a singlet radical pair generated in the photo-Fries rearrangement.[9] A greater degree of translational motion was observed for singlet and triplet benzyl radical pairs produced on silica gel by photolysis of a benzyl phenylacetate and a dibenzyl ketone, respectively.[5] The radical mobility was affected by both the radical pair multiplicity and the photolysis temperature. Radical pairs generated by photolysis of azocumene[10] and diacyl peroxides[11] on silica gel have also exhibited substantial surface mobility, although decomposition of the latter is, apparently, complicated by the intervention of ionic processes. The observations of ^{13}C enrichment and of rearranged starting materials in the photolysis of adsorbed dibenzyl ketone[12] indicated that the silica surface was considerably more effective than a solvent cage in restricting radical motion on the shorter time scale of the benzyl–phenylacetyl radical pair. Previously undetected products formed by photolysis of benzoin methyl ether on silica gel also provided evidence for restrictions on the mobility of adsorbed radicals.[6]

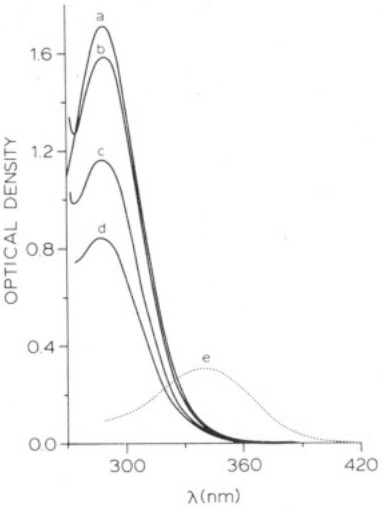


Figure 1. UV absorption spectra: (a) ketenimine **3** in benzene; (b–d) ketenimine **3** in a benzene–silica gel slurry at 0, 25, and 75 min after preparation; (e) 0.1578 M AIBN/benzene.

The solution thermolysis[17] and photolysis[19–21] of AIBN have been extensively studied. Loss of nitrogen produces two cyanopropyl radicals which couple to produce tetramethylsuccinodinitrile (**2**) and dimethyl-*N*-(2-cyano-2-propyl)ketenimine (**3**) and disproportionate to give isobutyronitrile (**4**) and methacrylonitrile (**5**) (Scheme I). The direct photolysis occurs efficiently (ϕ ~0.45 in benzene[21]) to give a product distribution (**2**, ~55%; **3**, ~40%; **4** and **5**, ~5% each) which is similar to that obtained by thermolysis and which varies little with solvent or temperature. Photolysis of other azoalkanes has been shown to occur by isomerization to a thermally unstable cis azo compound which then decomposes.[22] However, McBride et al.[20] have found no evidence for the formation of a cis isomer during low-temperature irradiation of **1** and have, thus, suggested that the direct decomposition of an AIBN excited state occurs (see, however, Table IV of ref 21). Engel et al.[21] have shown that the photodecomposition of AIBN can be induced by a variety of triplet sensitizers. It remains to be demonstrated whether direct decomposition of a triplet state of photoisomerization to a thermally labile cis isomer is responsible for the triplet-sensitized photolysis of AIBN.

McBride et al.[20] have also found that in the photolysis of crystalline AIBN 70–90% of the products arises from disproportionation. The results were not interpretable on the basis of the viscosity of the medium but were rationalized in terms of the intervention of intermolecular dipolar interactions.

It has been reported, however, that photolysis of AIBN in a silica gel–benzene slurry led only to the formation of **2**;[23] it was claimed, in explanation, that the cyanopropyl

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radicals were bound to the surface's active sites and were not free to rotate and so did not produce the unsymmetrical coupling product, ketenimine **3**, as occurs in solution. These facts and their interpretation appear to have been generally accepted.[20,24] However, in view of the results obtained for adsorbed radicals referred to already, it appeared unlikely that the silica gel could impose such severe restraints upon the rotational motion of cyanopropyl radicals. We report here results which require revision of the earlier proposals[23] and which demonstrate that both rotational and translational movement of cyanopropyl radicals occur. A preliminary account of part of this work has been given.[25]

Results and Discussion

Stability of Ketenimine 3 on Silica Gel. The stability of ketenimine **3** on silica gel was first examined to ensure that conversion of **3** to **2**, either thermally[26] or photochemically, would not be a complication in the photolysis of adsorbed AIBN. First, silica gel was added to a 0.113 M benzene solution of **3** in a 1-mm cuvette. The ketenimine absorption (at 290 nm) decreased gradually (Figure 1), indicating that **3** was not stable in the silica gel–benzene slurry. Similarly, addition of silica gel to a cuvette containing a benzene solution solution of AIBN which had been irradiated to produce **3** resulted in a gradual decrease in the ketenimine absorption. Irradiation of AIBN in a silica gel–benzene slurry showed only a small increase in absorption at 290 nm, although the absorption at 360 nm, due to AIBN, decreased as expected.

The nature of the products formed from **3** adsorbed on silica gel was then determined. Silica gel was added to a benzene solution of ketenimine, and the resulting slurry was left in the dark at room temperature for 12 h. The material extracted from the slurry was shown to be unchanged **3** (55%) and its hydrolysis product, *N*-(1-cyano-1-methylethyl)isobutyramide (**6**, 45%;[27] Scheme I). Substantial amounts of ketenimine hydrolysis were observed under various conditions; for example, on silica gel dried at 200 °C under vacuum before addition of **3** there was still >30% hydrolysis. In all cases the isolated amide accounted quantitatively for the amount of ketenimine decomposition.

Ketenimine **3** has been reported to be stable when irradiated in benzene through Pyrex with a 450-W Hanovia medium-pressure mercury arc.[20] Its stability to irradiation in a silica gel–benzene slurry was examined to test for the formation of additional products under these conditions. After irradiation of **3** in a slurry for 4 h, the material extracted was 27% amide and 70% ketenimine. No additional products were detected. Furthermore, the rate of decomposition of **3** in a slurry was followed spectrophotometrically for two samples, one of which was kept in the dark while the second was irradiated (Pyrex). The ketenimine absorption for both decreased at approximately the same rate. These experiments indicated that irradiation of **3** gave no additional decomposition products and did not influence the rate of hydrolysis.

Photolysis of AIBN in Silica Gel–Benzene Slurries. Irradiation of AIBN in a silica gel–benzene slurry gave the dinitrile **2** with, contrary to earlier reports,[23] substantial amounts of the unsymmetrical coupling product, ketenimine **3**, together with the amide derived from it. In general, the sum of **3** and **6** represented ~50% of the isolated products (Table I). These results were similar to those obtained for photolysis in solution except for the added feature of ketenimine hydrolysis. Analysis of the supernatant benzene layer showed that, prior to irradiation, a substantial amount (15–20%) of the azo compound was present in the solvent. It is, therefore, probable that some photolysis occurred in the solvent phase. In any event, the silica gel clearly provides little restriction to the rotational motion of cyanopropyl radicals.

Table I. Photolysis of AIBN in Silica Gel–Benzene Slurries and on Dry Silica Gel

conditions[a]	temp, °C	product distribution, mol % 29	30	33
slurry, A, C	20	43	16	41
slurry, A, C	20	48	13	38
slurry, A, C	40[b]	57	2	43
slurry, A, D	20	50	13	37
slurry, B, C	20	55	14	30
slurry, B, C	52[b]	58		52
slurry, B, D	20	59	34	7
slurry, A, F, D	10	62		38
slurry, A, F, E	10	66		33
dry silica gel (G),[c] A, C	10	53	16	31
dry silica gel (G),[c] A, C	10	58	13	29
dry silica gel (H),[c] A, C	10	63	25	12
dry silica gel (H),[c] A, C	10	73	9	17

[a] A, medium-pressure Hanovia Hg lamp; B, high-pressure Hg lamp (shorter irradiation time); C, Corning 7-60 filter ($\lambda > 330$ nm); D, Pyrex filter; E, quartz filter; F, immersion well. [b] <5% dark decomposition of AIBN to **2** occurred under these conditions. [c] Coverages were 0.403 mmol AIBN/g (G) and 0.0812 mmol/g (H).

The photolysis of AIBN in a slurry under a variety of conditions was undertaken to determine whether or not the incompatibility of the present results with those obtained previously was caused by changes in the (inadequately) reported experimental procedure.[23] The data presented in Table I show that, except for variations in the amount of hydrolysis of **3**, similar product ratios were obtained in all cases. Changes in light intensity, irradiation temperature variations, or the use of a Pyrex instead of a 330-nm cut-off filter had little effect. Two large-scale photolyses of AIBN in silica gel–benzene slurries in an immersion well, using either a Pyrex or quartz filter, both yielded substantial amounts of amide **6**. It was, therefore, concluded that the earlier observations[23] were in error; the unsymmetrical ketenimine was, indeed, formed upon photolysis of AIBN in a slurry and was partially hydrolyzed to the corresponding amide on the silica gel surface. The product ratios indicate that the surface does not restrict the rotational movement of the radicals to a much greater extent than does a solvent cage.

Photolysis of AIBN on Silica Gel. Samples of AIBN adsorbed on dry silica gel at two coverages (25% and 5%, by calculation) were irradiated. The product distributions (Table I) were qualitatively similar to those obtained in the slurry experiments, with some hydrolysis of **3** again being observed.

The normal isolation procedure used in these and the previous experiments would have resulted in the loss of volatile compounds such as **4** and **5**. A specific search for these among the products from irradiation of AIBN on dry silica gel at 25% coverage was, therefore, made and showed the presence of ~5% **4**. The similarity of the surface

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Table II. Mass Spectral Peak Intensities for Amide 6 from the Direct Photolysis of Equimolar Mixtures of AIBN-d_0 and AIBN-d_{12}

	intensities[a]		
conditions	*m/e* 154	*m/e* 160	*m/e* 166
benzene	84.7	47.2	100
silica gel, 25% coverage[b]	82.6	11.5	100
silica gel, 25% coverage	89.7	18.7	100
silica gel, 25% coverage	74.9	17.1	100
silica gel, 25% coverage	76.0	14.2	100
silica gel, 25% coverage	84.5	17.0	100
silica gel, 5% coverage[c]	83.0	15.8	100
silica gel, 5% coverage	88.6	16.2	100
silica gel–benzene slurry	90.9	23.0	100
silica gel–benzene slurry	91.5	27.5	100

[a] Corrected for the secondary isotope effect on the mass spectral fragmentation. Error limits, ±0.5–0.8. [b] 0.403 mmol/g. [c] 0.0812 mmol/g.

product ratios to those in solution and their difference from the results obtained for crystalline AIBN indicate that restrictions to rotational motion on silica gel are not severe.

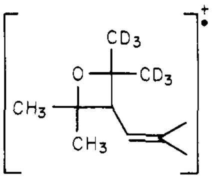
Geminate Recombination of Cyanopropyl Radicals. The amount of nongeminate radical combination was used as a measure of the translational movement of cyanopropyl radicals on silica gel. The fraction of nongeminate combination was determined by photolysis of equimolar mixtures of deuteriated and undeuteriated AIBN followed by analysis of the products for deuterium content. If only geminate radical recombination occurred, then only R_H–R_H and R_D–R_D coupling products would result. Conversely, complete nongeminate combination would lead to free $R_H\cdot$ and $R_D\cdot$ which would yield a statistical mixture (1:2:1) of R_H–R_H, R_H–R_D, and R_D–R_D. The presence of partially deuteriated products would show that some translational radical motion had occurred.

The demonstration of translational motion of adsorbed radicals using the above approach requires that the partially deuteriated products not result from simultaneous photolysis of adjacent azoalkane molecules. The intensity of the lamp used for irradiation of adsorbed AIBN was such that the probability of a photon striking an adjacent molecule during the lifetime of a cyanopropyl radical pair was negligible ($\ll 1\%$). It may, therefore, be concluded that photolysis of nearest neighbors was not a complication in these experiments.

Deuteriated azobis(isobutyronitrile) was prepared from acetone-d_6;[20] equimolar mixtures of AIBN-d_0 and AIBN-d_{12} were then photolyzed. The symmetrical coupling product, 2, did not yield a measurable molecular ion peak and was, therefore, unsuitable for mass spectral deuterium analysis. The unsymmetrical ketenimine, 3, also gave a weak molecular ion and was difficult to separate from other products because of its propensity for hydrolysis and thermal decomposition. Consequently, the amide derived from 3 was separated from unreacted AIBN and the other products and its deuterium content determined by mass spectral analysis (M^+ ~20% of base peak intensity).

A mixture of AIBN-d_0 and AIBN-d_{12} was first photolyzed in benzene so that the amount of geminate recombination in solution could be compared to that on silica gel. The mass spectral molecular ion intensities at *m/e* 154 (6), 160 (6-d_6), and 166 (6-d_{12}) were obtained in the ratio of 65.1:41.4:100. This result clearly demonstrated that a substantial number of cyanopropyl radicals did not recombine with their original germinate radical partners in solution. However, the rather larger discrepancy between the amount of 6-d_0 and 6-d_{12} was unexpected; one possible interpretation was that a secondary isotope effect on the mass spectral fragmentation was, at least partially, responsible.

To test for such a possibility, we prepared the deuteriated amide by hydrolysis of ketenimine formed from photolysis of AIBN-d_{12}. The mass spectral molecular ion intensities were then measured for an equimolar mixture of 6-d_0 and 6-d_{12}. The ratio of 74.7:100.0 obtained (average of three determinations, 20 eV) indicated that there was indeed a substantial isotope effect on the mass spectral fragmentation of amide 6. Although this corresponds to a total isotope effect of $(k_H/k_D)_T = 1.34$, the effect per atom is small, $(k_H/k_D)_T^{1/2} = 1.02$. Similar secondary deuterium isotope effects have been reported for mass spectral fragmentations of, for example, the oxetane 7 molecular ion[28] (k_H/k_D = 1.03/atom at 20 eV) and the enolic acetone ion 8[29] (k_H/k_D = 1.10/atom).



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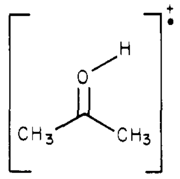

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All mass spectral deuterium analysis data were corrected for the observed isotope effect so that the intensities could be related to the relative amounts of 6-d_0, 6-d_6, and 6-d_{12}. For photolysis of the equimolar mixture of AIBN-d_0 and AIBN-d_{12} in benzene the ratio of intensities at *m/e* 154, 160, and 166 after correction was 84.7:47.2:100 (Table II): a substantial number of radicals geminate recombination under these conditions.

Equimolar mixtures of AIBN-d_0 and AIBN-d_{12} were photolyzed on silica gel at two coverages (25% and 5%). The corrected mass spectral peak intensities for the amide recovered after photolysis are listed in Table II. The amount of partially deuteriated amide formed by nongeminate radical combination decreased considerably from that obtained in benzene. For example, at 25% coverage the average ratio of 6-d_0/6-d_6/6-d_{12} was 81.5:15.7:100; changing the coverage to 5% had little effect on the amide ratios. Mixtures of deuteriated and undeuteriated azo compound were also photolyzed in silica gel–benzene slurries. The fraction of amide 6-d_6 increased slightly from that on dry silica but was still much lower than in benzene. This increase in escape from the original geminate partner was most likely caused by some photolysis in the solvent phase for the slurry experiments; however, the similar amounts of 6-d_6 formed on dry silica and in a slurry suggested that, for the latter, most of the photolysis had occurred for adsorbed molecules.

The above results may be more easily compared with each other and with other work by calculating the fraction of geminate recombination, β, by using eq 1. The corrected mass spectral peak intensities at *m/e* 154, 160, and 166 are used to obtain [6-d_0], [6-d_6], and [6-d_{12}], respectively. β is defined as one minus the fraction of products formed by escape from the original geminate partner. Values of β in benzene, on silica gel, and in silica gel–

$$\beta = 1 - \frac{2[\mathbf{6}\text{-}d_6]}{[\mathbf{6}\text{-}d_0] + [\mathbf{6}\text{-}d_6] + [\mathbf{6}\text{-}d_{12}]} \qquad (1)$$

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Table III. Fraction of Geminate Recombination, β, for Photolysis of AIBN

conditions[a]	β	β(corr)[b]
benzene, A	0.59	
benzene + sensitizer, B	0.13	0.10
benzene + sensitizer, B	0.19	0.16
silica gel, 25% coverage,[c] B	0.84	
silica gel, 5% coverage,[d] B	0.84	
silica gel + sensitizer, B	0.31	
silica gel + sensitizer, B	0.31	
silica gel + sensitizer, C	0.78	

[a] A, Corning 7-60 filter ($\lambda > 330$ nm); B, $NiSO_4$ and K_2CrO_4 filters; C, Corning 5-60 filter ($\lambda > 335$ nm). [b] Corrected for direct photolysis. [c] Average of five determinations. [d] Average of two determinations.

benzene slurries are listed in Table III.

For photolysis in benzene the β value of 0.59 agrees well with the cage effect of 0.61 reported previously for photolysis of a similar azo compound, azobis(3-methyl-1-butene).[21] For photolysis on dry silica gel and in silica gel–benzene slurries the substantially higher β values of 0.84 and 0.76 indicate that fewer radicals escape from their original partners before recombining. The silica gel surface must, therefore, restrict the translational motion of cyanopropyl radicals to a greater extent than it does their rotational movement. Nevertheless, ~15% of the radicals have sufficient mobility to escape from their original geminate partners. There is no evidence for restriction to radical movement by molecules of azobis(isobutyronitrile) itself, since the β values are identical over the coverage range used.

Triplet-Sensitized Photolysis of AIBN. A variety of triplet sensitizers have been shown to sensitize the photodecomposition of AIBN.[21] It was expected that substantial decreases in the fraction of geminate recombination would be observed for the sensitized photolysis on silica gel and in benzene if, as has been suggested, direct decomposition of a triplet state occurs in the sensitized photolysis of azo compounds. Decreased cage effects have been previously observed by Engel for the sensitized photolysis of azobis(3-methyl-1-butene).[21]

Benzophenone was used as the sensitizer for the silica gel reactions because it has a moderate quantum yield for sensitization ($\Phi = 0.10$) in solution and is less volatile than some of the other sensitizers which could have been used (e.g., acetophenone, $\Phi = 0.14$). Before attempting the sensitized photolysis on the surface, both AIBN and an equimolar mixture of AIBN-d_0 and AIBN-d_{12} were photolyzed in benzene in the presence of benzophenone. The product ratios from AIBN in the sensitized experiment were similar to those for the direct photolysis. For the mixture of AIBN-d_0 and AIBN-d_{12} the mass spectral molecular ion intensities were as shown in Table IV. The intensity ratios (145:165:100 for the peaks at m/e 154, 160, and 166 for one experiment) indicated a dramatic increase, relative to direct photolysis, in the amount of product formed by escape from the solvent cage. A β value of 0.19 may be calculated from the data (Table III) which, after correction for relative light absorption and the quantum yields of direct and sensitized photolysis, gives a corrected β value of 0.13 (average) for the triplet reaction: only ~13% of the radicals recombine in the solvent cage. Similar values (0.07–0.13, depending on the sensitizer) were obtained previously for the cage effect in the sensitized photolysis of azobis(3-methyl-1-butene).[21]

The results obtained provide support for the proposed[21] direct decomposition of triplet azo compounds in the sensitized photolysis of AIBN and other azoalkanes. If triplet-sensitized isomerization to an unstable cis isomer which subsequently decomposed thermally were occurring, the amount of cage recombination would be expected to be similar to that obtained by direct photolysis; i.e., thermal decomposition of the cis isomer would generate a singlet radical pair as would direct photolysis (regardless of whether the latter process proceeds via direct decomposition of a singlet or via isomerization to a thermally labile cis isomer). The different cage effects for direct and sensitized photolysis are, thus, attributed to the generation of radical pairs of different multiplicities in the two processes.

Table IV. Mass Spectral Peak Intensities for Amide 6 from the Triplet-Sensitized Photolysis of Equimolar Mixtures of AIBN-d_0 and AIBN-d_{12}

	intensities[b]		
conditions[a]	m/e 154	m/e 160	m/e 166
benzene,[c] B	143	186	100
benzene,[c] B	145	166	100
silica gel, B	129	120	100
silica gel, B	121	116	100
silica gel, C	106	25	100

[a] B, $NiSO_4$ and K_2CrO_4 filters; C, Corning 5-60 filter ($\lambda > 355$ nm). [b] Corrected for the secondary isotope effect on the mass spectral fragmentation. [c] 0.0314 M 28 and 0.124 M benzophenone.

For the sensitized photolysis of AIBN on silica gel the benzophenone and azo compound coverages were ~34% and ~7%, respectively (by calculation). The recovered amide contained a much larger amount of the partially deuteriated material than had been obtained by direct irradiation. For example, a ratio of 129:120:100 was obtained in one experiment, giving a β value of 0.31. Again, as for solution, some decomposition is expected to result from the direct photolysis of AIBN. However, the β values could not be corrected for direct photolysis on the surface since neither the extinction coefficients for AIBN and benzophenone nor the relative quantum yields for the direct and sensitized processes under these conditions were known. In any case, the results, even without correction, demonstrate that a large number of radicals recombine with other than their original partners in the triplet reaction. Correction for direct singlet photolysis would only further increase the number.

It is tempting to attribute the difference between the direct and sensitized experiments on the surface to the already discussed multiplicity difference, and consequent behavior, in the radical pairs formed by the two pathways. Nevertheless, the possibility that the effects could be caused by the benzophenone acting as a surface "additive"[30] rather than, or in addition to, a sensitizer must also be considered. For example, if the sensitizer occupied strong adsorption sites on which the azo compound would otherwise have been adsorbed, then the cyanopropyl radicals would be more translationally mobile, and a smaller amount of geminate recombination would result than in the absence of benzophenone. Similar effects of surface additives have been observed previously.[10,30]

To test for such a possibility, we photolyzed a sample of benzophenone and AIBN-d_0 plus AIBN-d_{12} on silica gel at (primarily) 366 nm in air. At this wavelength most of the light is absorbed by the AIBN and, in the presence of oxygen, most of any benzophenone triplets formed should be quenched before energy transfer to AIBN could occur. The recovered amide showed peaks at m/e 154, 160, and

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(30) Bauer, R. K.; de Mayo, P.; Ware, W. R.; Wu, K. C. *J. Phys. Chem.* **1982**, *86*, 3781.

166 in a ratio of 106:26:100 (Table IV); a β value of 0.78 was calculated. This is only slightly lower than the value of 0.84 obtained by direct photolysis. The difference may result from the occurrence of some sensitized photolysis in this experiment or, alternatively, it may, indeed, be derived from some effect of benzophenone as an additive. In any event, the results demonstrate that the primary role of benzophenone on the silica gel surface is that of a sensitizer and that the increased amount of geminate recombination in the presence of benzophenone reflects the triplet nature of the cyanopropyl radical pair as observed previously for benzyl radicals.[5] The larger β value for the triplet reaction on silica gel as compared to that in solution reflects the increased restrictions to translational radical motion on the surface.

For both the singlet and triplet reactions in benzene and on the silica gel surface nonequivalent amide-d_0 amide-d_{12} ratios were always obtained. Furthermore, the amount of **6**-d_{12} was greater than that of **6**-d_0 for the direct irradiations whereas the opposite trend was observed for the sensitized experiments. These effects may be a reflection of the larger hyperfine interaction in the nondeuteriated cyanopropyl radicals; d_0 radicals undergo more rapid hyperfine coupling induced intersystem crossing than do d_6 radicals. As a result, a singlet radical pair generated from AIBN-d_0 will intersystem cross more quickly to a triplet pair and will have a greater probability of diffusing apart than will a pair generated from AIBN-d_{12}. The opposite will occur for triplet radical pairs; a nondeuteriated pair will recombine with its original partner more often than will a pair generated from AIBN-d_{12}. A greater percentage of geminate recombination will, thus, occur for singlet d_6 radical pairs than for singlet d_0 pairs; for triplet pairs, geminate recombination for d_0 pairs will be larger than for d_6 pairs.

The above explanation is consistent with the larger amounts of **6**-d_{12} and **6**-d_0 in the direct and sensitized experiments, respectively. However, it requires that there be a similar nonequivalence in the amounts of another deuteriated and nondeuteriated product. For example, there could be a difference in the ratios of carbon–carbon to carbon–nitrogen coupling for geminate and free-radical recombination. If carbon–carbon coupling were increased for free radicals, then, for the singlet reaction, the **2**-d_0/**2**-d_{12} ratio should be >1 since there are more free R-d_0 radicals. Alternatively, the probability of disproportionation to yield **4** and **5** could be different for geminate and free-radical recombination. The ~5% disproportionation observed both in solution and on silica gel for the singlet photolyses would be sufficient to account for the nonequivalent amide-d_0 and -d_{12} ratios in these experiments. The amounts of disproportionation in the sensitized reactions have not been determined. A small amount of an undetected product could also be important in either the cage of escape radical processes (mass balances on silica gel are typically ~90%).

Conclusions

These may be summarized as follows: (a) the previously reported observations implying that the cyanopropyl radical is anchored by the nitrile function is incorrect; (b) the cyanopropyl radical can escape, by translational motion, from its geminate partner to a greater or lesser degree depending on the multiplicity of the radical pair; (c) the mechanism of triplet-sensitized decomposition of azoalkanes is most probably via direct photolysis and not via an isomerization to the cis isomer followed by thermal breakdown.

Experimental Section

Equipment. UV spectra were recorded on a Varian Cary 219 spectrophotometer. Proton NMR spectra were recorded on either a Varian T-60 (60 MHz) or XL-100 (100 MHz) spectrometer with tetramethylsilane as the internal standard. Mass spectra were measured on a Varian MAT 311A mass spectrometer. Melting points were measured on a Reichert hot stage and are uncorrected. Irradiations were carried out with a 450-W Hanovia medium-pressure lamp or a 100-W high-pressure mercury lamp with the following filters: Pyrex; Corning 7-60 ($\lambda > 330$ nm); Corning 5-60 ($\lambda > 355$ nm); or an inner $NiSO_4$ filter (250 g/L, 1.6-cm path length) plus an outer K_2CrO_4 filter (0.27 g/L of K_2CrO_4, 1 g/L of Na_2CO_3, 1-cm path length).

Materials. Silica gel (35–70 mesh, Merck) was used as received. Benzene and methylene chloride were spectrograde; for the sensitized solution photolyses benzene was refluxed over lithium aluminum hydride and then distilled through a 6-in. column. Azobis(isobutyronitrile) was recrystallized several times from ethanol at ≤50 °C (mp 101.5–102.5 °C). Benzophenone was recrystallized twice from hexane. Azobis(isobutyronitrile)-d_{12} was prepared by the literature procedure[20] for the preparation of the undeuteriated material[31] (mp 107–108 °C; mass spectrum, 97.8% d_6, 2.2% d_5, 99.6 atom % enrichment). Dimethyl-*N*-(2-cyano-2-propyl)ketenimine was prepared by photolysis of AIBN in benzene and was purified by removal of tetramethylsuccinodinitrile by precipitation from cyclohexane followed by repeated distillation. *N*-(1-cyano-1-methylethyl)isobutyramide was prepared by hydrolysis of ketenimine **3** and was recrystallized from benzene (mp 106–107 °C).[27] *N*-(1-Cyano-1-methylethyl)isobutyramide-d_{12} was prepared by hydrolysis of **3**-d_{12} obtained from photolysis of AIBN-d_{12} and was recrystallized from benzene (mp 105–106 °C).

Photolysis in Silica Gel–Benzene Slurries. Slurries were prepared by adding a benzene solution of AIBN to a weighed sample of silica gel in a test tube (0.281 mmol/g of silica gel/2.0 mL of benzene). The test tubes were closed with a rubber septum. The samples were stirred and irradiated with the lamps and filters indicated in Table I. Samples were either cooled with air (20 °C experiments) or placed in a water bath (40, and 52 °C experiments) during irradiation. The material was extracted with ~100 mL of diethyl ether. After solvent removal on a rotlary evaporator, dibenzyl was added as an internal standard, and the sample was dissolved in $CDCl_3$ and analyzed by NMR. The amounts of each compound present were determined from the known amount of standard added and the average of three integrations. In some cases the solvent was removed and the sample was redissolved in C_6D_6 and reanalyzed by NMR; since some signals were better resolved in C_6D_6, this provided an added check for the analysis.

Photolysis on Dry Silica Gel. (1) Direct. Azobis(isobutyronitrile) was adsorbed on silica gel at two coverages; 0.403 and 0.0812 mmol/g of silica gel. These correspond to 25% and 5% monolayer coverage, respectively, based on the calculated value of 1.7 mmol/g for 100% monolayer coverage. This number was calculated from the surface area of the silica gel (560 m^2/g) and the molecular area of AIBN (~0.55 nm^2, fro mspace-filling molecular models).

The following adsorption procedure was used for the preparation of dry silica gel samples. An appropriate amount of a methylene chloride solution of AIBN was added to a weighed silica gel sample in a round-bottomed flask. The solvent was evaporated, and the sample was transferred to a Pyrex irradiation tube and evacuated. The sample was then degassed (10^{-5} torr) at liquid nitrogen temperature, and the tube was filled with oxygen-free nitrogen and sealed. The rotated tube was cooled with running water and irradiated with the 450-W lamp (7–60 filter) for from 2 to 10 h, depending on the coverage and the required conversion. The adsorbed material was extracted with 100 mL of ether; after solvent removal, the mixture was analyzed as describes previously.

(2) Benzophenone Sensitized. Benzophenone (0.441 mmol/g of silica gel; 34% coverage based on a molecular area of 0.71 nm^2) was adsorbed first followed by AIBN (0.117 mmol/g of silica gel; 7% coverage) by using the above adsorption procedure. The

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[31] (a) Overberger, C. G.; O'Shaugnessy, M. T.; Shalit, H. *J. Am. Chem. Soc.* **1949**, *71*, 2661. (b) Dox, A. W. *Ibid.* **1925**, *47*, 1471.

sample was degassed at room temperature ($\leq 10^{-5}$ torr) for 2 h; oxygen-free nitrogen was then added, and the tube was sealed. The rotated tube was irradiated at 12 ± 2 °C with the 450-W lamp ($NiSO_4$, K_2CrO_4 filters) for ≥20 h. Product extraction and analysis were as previously described.

Solution Photolysis. For direct irradiation experiments solutions of AIBN in benzene were deaerated by purging with nitrogen for 20 min and were then irradiated at 20 °C (air cooling) with the 450-W lamp (7-60 filter). Samples of AIBN plus benzophenone (0.0314 and 0.124 M, respectively) were degassed ($\leq 10^{-5}$ torr) by four freeze–thaw cycles at 77 K and were then sealed. The samples were irradiated with the 450-W lamp ($NiSO_4$, K_2CrO_4 filters) at 12 ± 2 °C. Products were analyzed by NMR as outlined above.

Ketenimine Hydrolysis. (1) UV Experiments. A slurry of dimethyl-*N*-(2-cyano-2-propyl)ketenimine was prepared by adding silica gel to a 1-mm cuvette containing a 0.113 M benzene solution of ketenimine. The mixture was stirred as much as possible to provide an even distribution of the adsorbate. The ketenimine decomposition was monitored by the decrease in its absorption band at 290 nm (Figure 1).

A 0.158 M AIBN solution (benzene) in a 1-mm cuvette was irradiated to ~50% conversion. The absorption due to ketenimine **3** decreased upon addition of silica gel to the cuvette. After 80 min the absorption at the 290-nm had decreased to ~$^1/_4$ of its original intensity.

Photolysis of AIBN in a silica gel–benzene slurry showed a gradual decrease in the absorption at 360 nm (AIBN) but only a small increase at 290 nm, even after extensive irradiation. The spectrum of the sample was unchanged after 12 h in the dark.

(2) Preparative Experiments. Silica gel (2.8 g) was added to 5 mL of 0.113 M benzene solution of **3**. The mixture was stirred thoroughly and then left at 25 °C in the dark for 12 h. The sample was extracted and analyzed as described previously and was shown to consist of amide **6** (45%) and unreacted **3** (55%). Similar experiments always resulted in substantial amounts of ketenimine hydrolysis. The amide was isolated from one experiment and its identity confirmed by comparison with an authentic sample.

Measurement of Geminate Recombination. Samples of an equimolar mixture of AIBN-d_0 and ABIN-d_{12} in benzene, in silica gel–benzene slurries, and on dry silica gel were prepared, degassed, and irradiated (to ≥50% conversion) as outlined in the preceding sections. Amide **6** was isolated from the reaction mixtures by chromatography on silica gel plates, with 10% methanol/benzene being used as the eluent. The deuterium content in the amide was determined by mass spectral analysis of the molecular ion region (m/e 154 (d_0), 160 (d_6) and 166 (d_{12})). The intensities at m/e 154 and 160, I_{154} and I_{160}, respectively, were corrected for the secondary isotope on the mass spectral fragmentation by using eq 2 and 3, where I' refers to the corrected intensity. A standard

$$I'_{154} = (k_H/k_D)_T{}^{1/12} \tag{2}$$

$$I'_{160} = [(k_H/k_D)_T{}^{1/12}]^6 \tag{3}$$

amide sample consisting of equimolar **6**-d_0 and **6**-d_{12} was run directly before each sample so that changes in the isotope effect due to instrumental variations did not affect the results. The corrected data were then used to calculate β from eq 1.

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Registry No. **1**, 78-67-1; **2**, 3333-52-6; **3**, 10551-67-4; **6**, 84213-57-0; 2-cyano-2-propyl radical, 3225-31-8.

Redox-Photosensitized Reactions. 11.[1] Ru(bpy)$_3{}^{2+}$-Photosensitized Reactions of 1-Benzyl-1,4-dihydronicotinamide with Aryl-Substituted Enones, Derivatives of Methyl Cinnamate, and Substituted Cinnamonitriles: Electron-Transfer Mechanism and Structure–Reactivity Relationships

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Reactions of 1-benzyl-1,4-dihydronicotinamide (BNAH) with aryl-substituted enones and derivatives of methyl cinnamate and cinnamonitrile (**1a–u**) are photosensitized by Ru(bpy)$_3{}^{2+}$ (bpy = 2,2′-bipyridine). The reduction of carbon–carbon double bonds commonly requires the substitution of either an electron-withdrawing aryl group or two phenyl groups at the β-carbon atom of **1**. With enones which possess one aryl substituent with no extra electron-withdrawing group at the β position, the photosensitized reactions result in no two-electron reductions but give 1:1 adducts (**4d–h**) along with half-reduced dimers of olefins (**3d** and **3g**) and a half-oxidized dimer of BNAH (**5**). The observed results can be easily interpreted by assuming the intervention of 1-benzyl-3-carbamoyl-1,4-dihydropyridin-4-yl radical (BNA·) and half-reduced species (·**1**-H) as key intermediates that are formed by mediated electron–proton transfer from BNAH to **1** in which Ru(bpy)$_3{}^{2+}$ acts as a one-electron shuttle upon photoexcitation in the initial electron transfer. Whether BNA· undergoes electron transfer to or a radical-coupling reaction with ·**1**-H depends on steric and electronic properties of ·**1**-H which should be affected by the substituents at the radical center. Mechanistic implications for thermal reactions of NADH models with olefins in the dark are briefly discussed on the basis of these observations.

The reduction of carbon–carbon double bonds by 1,4-dihydropyridines (eq 1) is of biological interest as a model

$$\underset{\mathbf{1}}{R^1R^2C{=}CR^3X} + NADH + H^+ \rightarrow \underset{\mathbf{2}}{R^1R^2CHCHR^3X} + NAD^+ \tag{1}$$

for enzymatic reductions of steroidal enones[2] and unsaturated fatty acids[3] involving the pyridine nucleotide co-

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[1] Part 9: Pac, C.; Kubo, J.; Majima, T.; Sakurai, H. *Photochem. Photobiol.* **1982**, *36*, 273. Part 10: Ishitani, O.; Pac, C.; Sakurai, H. *J. Org. Chem.* **1983**, *48*, 2941.

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